PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification [6] :
A62C 2/00, 3/00, A62D 1/00, 1/02, 1/06, 1/08

A1

(11) International Publication Number: WO 96/10443

(43) International Publication Date: 11 April 1996 (11.04.96)

(21) International Application Number: PCT/US95/12602

(22) International Filing Date: 29 September 1995 (29.09.95)

(30) Priority Data:
08/316,406 30 September 1994 (30.09.94) US

(71) Applicant: THE UNIVERSITY OF NEW MEXICO [US/US]; Albuquerque, NM 87131 (US).

(72) Inventors: DIERDORF, Douglas, S.; 4614 Larchmont Drive N.E., Albuquerque, NM 87111 (US). SKAGGS, Stephanie, R.; 11301 Richfield N.E., Albuquerque, NM 87122 (US). TAPSCOTT, Robert, E.; 3812 Palomas Drive N.E., Albuquerque, NM 87110 (US). KAIZERMANN, Jacob; 507 1/2 Freeman N.W., Albuquerque, NM 87107 (US).

(74) Agent: BECKER, Robert, W.; Robert W. Becker & Associates, Suite 200, 5300 Sequoia N.W., Albuquerque, NM 87120 (US).

(81) Designated States: European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published
With international search report.

(54) Title: PHOSPHORUS NITRIDE AGENTS TO PROTECT AGAINST FIRES AND EXPLOSIONS

(57) Abstract

A set of phosphorus nitride agents for extinguishment of fires, suppression of explosions, and inertion against fires and explosions is disclosed. The agents have direct covalent bonds between phosphorus and nitrogen. Specifically disclosed are agents based on phosphorus nitride cyclic compounds and phosphorus nitride linear compounds and polymers.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria
AU	Australia
BB	Barbados
BE	Belgium
BF	Burkina Faso
BG	Bulgaria
BJ	Benin
BR	Brazil
BY	Belarus
CA	Canada
CF	Central African Republic
CG	Congo
CH	Switzerland
CI	Côte d'Ivoire
CM	Cameroon
CN	China
CS	Czechoslovakia
CZ	Czech Republic
DE	Germany
DK	Denmark
ES	Spain
FI	Finland
FR	France
GA	Gabon
GB	United Kingdom
GE	Georgia
GN	Guinea
GR	Greece
HU	Hungary
IE	Ireland
IT	Italy
JP	Japan
KE	Kenya
KG	Kyrgystan
KP	Democratic People's Republic of Korea
KR	Republic of Korea
KZ	Kazakhstan
LI	Liechtenstein
LK	Sri Lanka
LU	Luxembourg
LV	Latvia
MC	Monaco
MD	Republic of Moldova
MG	Madagascar
ML	Mali
MN	Mongolia
MR	Mauritania
MW	Malawi
NE	Niger
NL	Netherlands
NO	Norway
NZ	New Zealand
PL	Poland
PT	Portugal
RO	Romania
RU	Russian Federation
SD	Sudan
SE	Sweden
SI	Slovenia
SK	Slovakia
SN	Senegal
TD	Chad
TG	Togo
TJ	Tajikistan
TT	Trinidad and Tobago
UA	Ukraine
US	United States of America
UZ	Uzbekistan
VN	Viet Nam

PHOSPHORUS NITRIDE AGENTS TO PROTECT AGAINST FIRES AND EXPLOSIONS

Government Rights

This invention was made under contract with the U.S. Government, which has certain rights therein.

Technical Field

The invention described and claimed herein is generally related to chemical agents used for fire extinguishment, explosion suppression, explosion inertion, and fire inertion and more particularly, to extinguishing, suppressing, and inerting phosphorus nitride agents that are replacements for halon fire and explosion suppressants and extinguishants. The production of halons has been eliminated or curtailed in many nations due to their impact on stratospheric ozone.

Background Art

The broad class of halocarbons consists of all molecules containing carbon and one or more of the following halogen atoms: fluorine, chlorine, bromine, and/or iodine. Halocarbons may also contain other chemical features such as hydrogen atoms, carbon-to-carbon multiple bonds, or aromatic rings. Haloalkanes, a subset of halocarbons, contain only single bonds between the carbon atoms. The use of certain haloalkanes as fire extinguishing agents has been known for many years.

For example, fire extinguishers containing carbon tetrachloride and methyl bromide were used in aircraft applications as early as the 1920s. Over a period of years the high toxicity of these compounds was recognized and they were replaced with less toxic compounds. Chlorobromomethane was used in aircraft applications from the 1950s to the 1970s. A major study of haloalkanes as fire extinguishing agents was conducted by the Purdue Research Foundation for the U.S. Army from 1947 to 1950 (FIRE EXTINGUISHING AGENTS, Final Report, Purdue University, 1950). Haloalkanes used for fire protection are often designated by the "halon numbering system." This system gives in order the number of atoms of carbon, fluorine, chlorine, and bromine in the molecule. Thus, for example, $CBrClF2$, whose chemical name is bromochlorodifluoromethane, is often referred to as Halon 1211.

The term "extinguishment" is usually used to denote complete elimination of a fire; whereas, "suppression" is often used to denote reduction, but not necessarily total

elimination, of a fire or explosion. These two terms are sometimes used interchangeably. There are four general types of halocarbon fire and explosion protection applications. (1) In total-flood fire extinguishment and/or suppression applications, the agent is discharged into a space to achieve a concentration sufficient to extinguish or suppress an existing fire. This is often, though not always, done by an automatic system, which detects the fire and then automatically discharges the extinguishing agent to fill the space with the concentration of a gaseous or an evaporated volatile liquid agent to the concentration needed to suppress or extinguish the contained fire. Total flooding use includes protection of enclosed, potentially occupied spaces such as computer rooms as well as specialized, often unoccupied spaces such as aircraft engine nacelles and engine compartments in vehicles. Note that the term "total flood" does not necessarily mean that the extinguishing or suppressing agent is uniformly dispersed throughout the space protected. (2) In streaming applications, the agent is applied directly onto a fire or into the region of a fire. This is usually accomplished using manually operated wheeled or portable units. A second method, which we have chosen to include as a streaming application, uses a "localized" system, which discharges agent toward a fire from one or more fixed nozzles. Localized systems may be activated either manually or automatically. (3) In explosion suppression, a halocarbon is discharged to suppress an explosion that has already been initiated. The term "suppression" is normally used in this application since the explosion is usually self-limiting. However, the use of this term does not necessarily imply that the explosion is not extinguished by the agent. In this application, a detector is usually used to detect an expanding fireball from an explosion, and the agent is discharged rapidly to suppress the explosion. Explosion suppression is used primarily, but not solely, in defense applications. (4) In inertion, a halocarbon is discharged into a space to prevent an explosion or a fire from being initiated. Often, a system similar or identical to that used for total-flood fire extinguishment or suppression is used. Inertion is widely used for protection of oil production facilities at the North Slope of Alaska and in other areas where flammable gases or explosive dusts may build up. Usually, the presence of a dangerous condition (for example, dangerous concentrations of flammable or explosive gases) is detected,

and the halocarbon is then discharged to prevent the explosion or fire from occurring until the condition can be remedied.

Thus, there are four fire and explosion protection applications covered by this disclosure:

1. Total-Flood Fire Extinguishment and Suppression
2. Streaming Fire Extinguishment and Suppression
3. Explosion Suppression
4. Explosion and Fire Inertion

The halogenated chemical agents currently in use for fire extinguishment (by total flooding or streaming), explosion suppression, explosion inertion, and fire inertion are generally bromine-containing haloalkanes. Such chemicals contain bromine, fluorine, and carbon (and, in at least one case, chlorine), contain no hydrogen atoms, and have only single bonds between atoms. These chemicals include Halon 1202 (CBr_2F_2), Halon 1211 ($CBrClF_2$), Halon 1301 ($CBrF_3$), and Halon 2402 ($CBrF_2CBrF_2$). Information on the most important of the existing halons are shown in Table I. The "CAS No." is the number assigned by the Chemical Abstract Services of the American Chemical Society to aid in identifying chemical compounds. Halon 1301 (bromotrifluoromethane) and Halon 1211 (bromochlorodifluoromethane) are the most widely used haloalkane fire extinguishing agents. Halon 1301 is widely used for total-flood fire extinguishment, explosion suppression, and inertion. Due to its higher boiling point and higher toxicity, Halon 1211 is usually not used in total-flood applications, but, it is widely used in streaming.

TABLE I. EXISTING HALONS.

Name	Formula	Halon No.	CAS No.	Boiling Point, °C
dibromodifluoromethane	CBr_2F_2	1202	75-61-6	24.5
bromochlorodifluoromethane	$CBrClF_2$	1211	353-59-3	-4
bromotrifluoromethane	$CBrF_3$	1301	75-63-8	-58
1,2-dibromotetrafluoroethane	$CBrF_2CBrF_2$	2402	124-73-2	47

Bromine-containing haloalkanes such as the existing halons operate as fire extinguishing agents by a complex chemical reaction mechanism involving the disruption of free-radical chain reactions, which are essential for continuing combustion. The existing halons are desirable as fire extinguishing agents because they are effective, because they leave no residue (i.e., they are liquids that evaporate completely or they are gases), and because they do not damage equipment or facilities to which they are applied.

Recently, however, halons, have come to be recognized as serious environmental threats due to their ability to cause stratospheric ozone depletion. In the United States, production of the existing halons (Halon 1201, Halon 1301, Halon 1211, and Halon 2402) stopped at the end of 1993.

Much research has gone on to find replacements for the existing halons for protection against fires and explosions; however, the search for halon replacements has been less than totally successful ("Pressure Mounts As Search for Halon Replacements Reaches Critical Phase," Chemical and Engineering News, September 19, 1994, pp. 29-32). Most of the agents now being promoted as halon replacements are hydrochlorofluorocarbons (HCFCs), hydrofluorocarbons (HFCs), and perfluorocarbons (FCs or PFCs). HCFCs, HFCs, and FCs (PFCs) appear to operate primarily by heat absorption, which is a less effective mechanism for most fire and explosion protection applications than the free radical chain disruption mechanism used by the existing halons. Thus, HCFCs, HFCs, and FCs (a family that we refer to as "first-generation" halon replacements) have a significantly decreased effectiveness compared to the halons now used for fire and explosion protection in most applications. Moreover, the HCFCs have a sufficiently large ODP that their production is restricted and will eventually be phased out under both the Montreal Protocol and the U.S. Clean Air Act. Finally, the HFCs and, in particular, the FCs have significant atmospheric lifetimes (usually on the order of years or even hundreds of years) and are believed to cause global warming. This may cause eventual restrictions on the HFCs and FCs.

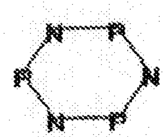
Accordingly, it is the object of the present invention to provide effective fire extinguishing, fire suppression, explosion suppression, and explosion and fire inertion agents that contain, as principal components, phosphorus nitride compounds. The

term "agent" here means either a single compound or mixtures of two or more compounds and may include mixtures of phosphorus nitride compounds with other materials.

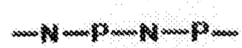
Disclosure of the Invention

The present invention provides phosphorus nitride compounds for use as agents for fire extinguishing and suppression (in either total-flooding or streaming application), explosion suppression, and explosion and fire inertion. As the term is used in this application, phosphorus nitride compounds are any compounds containing a direct (covalent) bond between a nitrogen atom and a phosphorus atom. Thus, they do not include such ionic compounds as ammonium phosphate (NH_4PO_4), where their is no direct bonding between nitrogen and phosphorus other than ionic attraction.

Phosphorus nitride compounds include two groups: cyclic compounds containing a cyclic backbone (usually containing alternating phosphorus and nitrogen atoms) and compounds having a backbone containing linear chains (but which also may contain cyclic substituents along the chain). The latter are often polymers whose exact structures have not been fully characterized. Examples are shown below for a six-member cyclic ring and for a four-member chain.



Cyclic



Chain

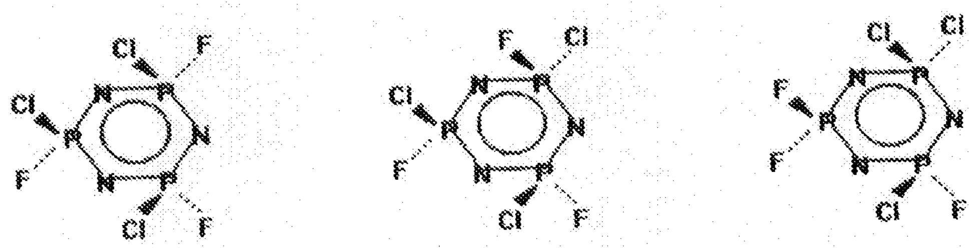
The backbones may contain substituents including but not limited to the halogens fluorine (F), chlorine (Cl), bromine (Br), and iodine (I); imino groups (=NH); alkyl and substituted alkyl groups; aryl and substituted aryl groups; and alkoxides. Alkyl groups are groups containing only carbon and hydrogen atoms such as methyl ($-CH_3$), ethyl ($-CH_2CH_3$), *n*-propyl ($-CH_2CH_2CH_3$), and *iso*-propyl ($CH(CH_3)_2$). Substituted alkyl groups are alkyl groups in which one or more of the hydrogen (H) atoms have been replaced by other atoms or groups. Examples are $-CH_2F$, $-CHF_2$, and $-CF_3$. Aryl groups are groups containing only carbon and hydrogen atoms in "aromatic" rings. The most common of these is the phenyl group, $-C_6H_5$. Substituted aryl groups have one or more of the hydrogen atoms replaced by some

other substituent. An example is perfluorophenyl, $-C_6F_5$. Alkoxide groups have the structure -OR, where R is an alkyl or a substituted alkyl group.

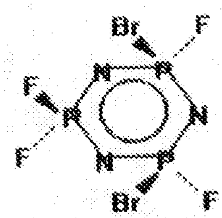
Cyclic Compounds

Agents include the cyclic phosporus fluoronitride compounds $P_3N_3F_6$, $P_4N_4F_8$, and, in general, cyclic compounds having a formula $(PNF_2)_n$, where "n" is 2 or greater. These compounds have the cyclic PN backbone with fluorine atoms as substituents. For example, the structures of the "trimer" $P_3N_3F_6$ and "tetramer" $P_4N_4F_8$ are shown below.

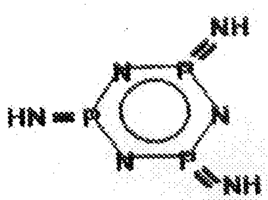
The compounds also include the cyclic phosphorus chloronitride compounds $P_3N_3Cl_6$, $P_4N_4Cl_8$, and, in general, cyclic compounds having a formula $(PNCl_2)_n$, where "n" is 2 or greater. Cyclic phosphorus nitrides containing both fluorine and chlorine in the same molecule are also included. Examples of trimers are $P_3N_3ClF_5$, $P_3N_3Cl_2F_4$, $P_3N_3Cl_3F_3$, $P_3N_3Cl_4F_2$, and $P_3N_3Cl_5F$. These include all isomers of the compounds. Isomers are different arrangements of the atoms on the same molecule. For example, three isomers available for $P_3N_3Cl_3F_3$ are shown below.



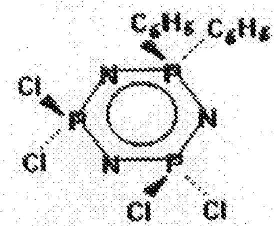
Bromine and iodine substituents may also be present. Cis-2,4-dibromo-2,4,6,6-tetrafluoro-1,3,5,2,4,6-triazaphosphorine is an example of a mixed fluorine/bromine substituted 6-membered ring:



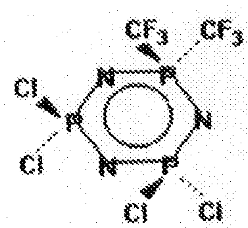
Examples of rings containing imino (=NH), aryl (here, phenyl, $-C_6H_5$), alkyl (here, trifluoromethyl, $-CF_3$), and alkoxy (here, methoxy, $-OCH_3$) are shown below.



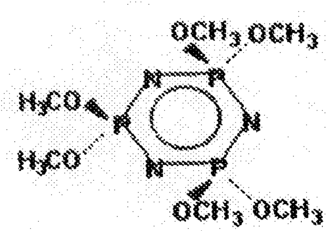
Phospham (Containing Imino Groups)



Containing Phenyl ($-C_6H_5$) Groups



Containing Trifluoromethyl ($-CF_3$) Groups



Containing Methoxy ($-OCH_3$) Groups

A list of some cyclic phosphorus nitride compounds is shown in Table II. The empirical formula gives the numbers of each type of atom without regard to actual structure. Thus, various isomers will all have the same empirical formula. The IUPAC name is the chemical name of the compound as assigned using rules established by the International Union of Pure and Applied Chemistry (IUPAC).

TABLE II. SELECTED CYCLIC PHOSPHORUS NITRIDES.

CAS No.	Empirical Formula	IUPAC Name	Boiling Point, °C
38589-76-3	$N_3P_3F_2Br_4$	(cis)-2,2,4,6-tetrabromo-4,6-difluoro-1,3,5,2,4,6-triazaphosphorine	
38589-81-0	$N_3P_3F_2Cl_4$	(cis)-2,2,4,6-tetrachloro-4,6-difluoro-1,3,5,2,4,6-triazaphosphorine	170
38589-72-9	$N_3P_3F_4Br_2$	(cis)-2,4-dibromo-2,4,6,6-tetrafluoro-1,3,5,2,4,6-triazaphosphorine	
38589-78-5	$N_3P_3Cl_2F_4$	(cis)-2,4-dichloro-2,4,6,6-tetrafluoro-1,3,5,2,4,6-triazaphosphorine	140
38589-74-1	$N_3P_3F_3Br_3$	(cis-cis)-2,4,6-tribromo-2,4,6-trifluoro-1,3,5,2,4,6-triazaphosphorine	
38589-79-6	$N_3P_3F_3Cl_3$	(cis-cis)-2,4,6-trichloro-2,4,6-trifluoro-1,3,5,2,4,6-triazatriphosphorine	
38589-75-2	$N_3P_3F_3Br_3$	(cis-trans)-2,4,6-tribromo-2,4,6-trifluoro-1,3,5,2,4,6-triazaphosphorine	
38589-80-9	$N_3P_3F_3Cl_3$	(cis-trans)-2,4,6-trichloro-2,4,6-trifluoro-1,3,5,2,4,6-triazatriphosphorine	
38589-77-4	$N_3P_3F_2Br_4$	(trans)-2,2,4,6-tetrabromo-4,6-difluoro-1,3,5,2,4,6-triazaphosphorine	
38589-83-2	$N_3P_3F_2Cl_4$	(trans)-2,2,4,6-tetrachloro-4,6-difluoro-1,3,5,2,4,6-triazaphosphorine	170
38589-73-0	$N_3P_3F_4Br_2$	(trans)-2,4-dibromo-2,4,6,6-tetrafluoro-1,3,5,2,4,6-triazaphosphorine	
38589-82-1	$N_3P_3F_4Cl_2$	(trans)-2,4-dichloro-2,4,6,6-tetrafluoro-1,3,5,2,4,6-triazaphosphorine	140

17022-78-5	$N_3P_3F_2Br_4$	2,2,4,4-tetrabromo-6,6-difluoro-1,3,5,2,4,6-triazaphosphorine	
21846-67-3	$N_3P_3F_2Cl_4$	2,2,4,4-tetrachloro-6,6-difluoro-1,3,5,2,4,6-triazaphosphorine	181.6
17022-77-4	$N_3P_3F_3Br_3$	2,2,4-tribromo-4,6,6-trfluoro-1,3,5,2,4,6-triazaphosphorine	
21846-68-4	$N_3P_3F_3Cl_3$	2,2,4-trichloro-2,4,6-trifluoro-1,3,5,2,4,6-triazatriphosphorine	150
17022-76-3	$N_3P_3F_4Br_2$	2,2-dibromo-4,4,6,6-tetrafluoro-1,3,5,2,4,6-triazaphosphorine	
21846-69-5	$N_3P_3Cl_2F_4$	2,2-dichloro-4,4,6,6-tetrafluoro-1,3,5,2,4,6-triazaphosphorine	114.7
17022-75-2	$N_3P_3F_5Br$	bromopentafluoro-1,3,5,2,4,6-triazaphosphorine	97
21846-70-8	$N_3P_3ClF_5$	chloropentafluoro-1,3,5,2,4,6-triazatriphosphorine	81
19258-92-5	$N_5P_5F_{10}$	decafluoro-1,3,5,7,9,2,4,6,8,10-pentazapentaphosphecine	120.1
19258-93-6	$N_6P_6F_{12}$	dodecafluoro-1,3,5,7,9,11-hexaaza-2,4,6,8,10,12-hexaphosphacyclododecahexaene	147.2
15599-91-4	$N_3P_3F_6$	hexafluoro-1,3,5,2,4,6-triazatriphosphorine	50
3880-04-4	$C_2H_6F_6N_2P_2$	hexafluoro-1,3-dimethyl-1,2,3,4-diazadiphosphetidine	91.6
14700-00-6	$N_4P_4F_8$	octafluoro-1,3,5,7,2,4,6,8-tetrazatetraphosphocine	89.7
13778-06-8	$N_3P_3FCl_5$	pentachlorofluoro-1,3,5,2,4,6-triazaphosphorine	215

Chain Compounds

In addition to cyclic rings, phosphorus/nitrogen compounds also form chains. One example of a simple linear molecule is $Cl_3P{=}N{-}PCl_2{=}NCl$. Phosphorus nitride chain compounds are often polymeric and contain a mixture of chains of different

lengths and may also contain some cyclic compounds within the mixture or attached to the chains. For example, when heated above 300°C, phosphorus fluoronitrides form colorless polymeric liquids. The polymeric liquids are believed to contain a mixture of chains of the type $F_3P{=}N\text{-}[PF_2{=}N]_n\text{-}PF_4$, where n is the number of repeating $PF_2{=}N$ units.

These and other aspects of the present invention will be more apparent upon consideration of the following detailed description of the invention.

Best Modes for Carrying out the Invention

The cup burner is a widely accepted laboratory test apparatus for determining the fire extinguishing and suppressing effectiveness of agents. In this method, an agent is introduced into a stream of air which passes around a cup of burning liquid fuel, and the concentration of gaseous agent needed to extinguish the flame is determined. During this operation, any agent that is normally a liquid is allowed to become a gas before being mixed into the stream of air and passed by the burning liquid fuel. The cup burner is so widely accepted that the National Fire Protection Association (NFPA) Standard 2001 on Clean Agent Fire Extinguishing Systems mandates this method as the primary procedure for determining the concentration needed to extinguish a fire of liquid hydrocarbon fuels (e.g., gasoline, hexane, etc; such fires are termed "Class B fires"). That standard states that "The minimum design concentration for Class B flammable liquids shall be a demonstrated extinguishing concentration plus a 20 percent safety factor. Extinguishing concentration shall be demonstrated by the cup burner test." Concentrations are usually expressed as "percent by volume." This is the same as the "percent by gas volume," which is calculated assuming that all of the introduced agent has volatilized (i.e., vaporized to become a gas).

A halocarbon carrier may be added to one or more of the phosphorus nitride compounds to aid in distribution of the agent, to modify the physical properties, or to provide other benefits. Mixtures of halocarbon carriers with phosphorus nitride compounds may be either azeotropes, which do not change in composition as they evaporate, or zeotropes, which do change in composition during evaporation (more volatile components tend to evaporate preferentially). Mixtures that change only slightly in composition during evaporation are sometimes termed "near azeotropes."

In some cases, there are advantages to azeotropes and near azeotropes. Mixtures covered by this application include azeotropes, near azeotropes, and zeotropes.

Carriers can be materials such as hydrochlorofluorocarbons, hydrofluorocarbons, or perfluorocarbons. Hydrochlorofluorocarbons (HCFCs) are chemicals containing only hydrogen, chlorine, fluorine, and carbon. Examples of HCFCs that could be used as carriers are 2,2-dichloro-1,1,1-trifluoroethane ($CHCl_2CF_3$), chlorodifluoromethane ($CHClF_2$), 2-chloro-1,1,1,2-tetrafluoroethane ($CHClFCF_3$), and 1-chloro-1,1-difluoroethane (CH_3CClF_2). Hydrofluorocarbons (HFCs) are chemicals containing only hydrogen, fluorine, and carbon. Examples of potential HFC carriers are trifluoromethane (CHF_3), difluoromethane (CH_2F_2), 1,1-difluoroethane (CH_3CHF_2), pentafluoroethane (CHF_2CF_3), 1,1,1,2-tetrafluoroethane (CH_2FCF_3), 1,1,1,2,2-pentafluoropropane ($CF_3CF_2CH_3$), 1,1,1,2,3,3-hexafluoropropane ($CF_3CHFCHF_2$), 1,1,1,3,3,3-hexafluoropropane ($CF_3CH_2CF_3$), 1,1,1,2,2,3,3-heptafluoropropane ($CF_3CF_2CF_2H$), 1,1,1,2,3,3,3-heptafluoropropane (CF_3CHFCF_3), and 1,1,1,4,4,4-hexafluorobutane ($CF_3CH_2CH_2CF_3$). Perfluorocarbons, which contain only fluorine and carbon, are characterized by very low toxicities. Examples of perfluorocarbons that could be used as carriers are tetrafluoromethane (CF_4), hexafluoroethane (CF_3CF_3), octafluoropropane ($CF_3CF_2CF_3$), decafluorobutane ($CF_3CF_2CF_2CF_3$), dodecafluoropentane ($CF_3CF_2CF_2CF_2CF_3$), tetradecafluorohexane ($CF_3CF_2CF_2CF_2CF_2CF_3$), perfluoromethylcyclohexane ($C_6F_{11}CF_3$), perfluorodimethylcyclohexane ($C_6F_{10}(CF_3)_2$), and perfluoromethyldecalin ($C_{10}F_{17}CF_3$). Our work indicates that some mixtures possess flame extinguishment and suppression ability greater than would be predicted from the intrinsic fire suppression ability of the separate components, a phenomenon that we term "synergism." Note that it is not necessary that the carrier have zero flammability. It is only necessary that the mixture of carrier(s) and phosphorus nitride agent(s) act as a fire and/or explosion protection agent.

The embodiments include the use of agents comprised of cyclic and/or linear (polymeric) phosphorus nitrides, with or without carriers, for the four applications of fire extinguishment or suppression using a total-flood application, fire extinguishment or suppression using a streaming application, explosion suppression, and inertion

against fires and explosions. The following examples illustrate the fire and explosion protection in accordance with the invention.

Example 1. Into a flowing air stream in which a cup of burning n-heptane fuel is contained was introduced a mixture of $N_3P_3F_6$, $N_3P_3F_5Cl$, $N_3P_3F_4Cl_2$, and $N_3P_3F_3Cl_3$ sufficient to raise the concentration to 0.28 percent agent by gas volume. This concentration of agent was less than one-tenth as much as required to extinguish the same fire using Halon 1211 (which required a concentration of 3.2 percent) or using Halon 1301 (which required a concentration of 2.9 percent).

Example 2. Onto a 1.5-inch diameter cup containing 1/4-inch of burning *n*-heptane fuel, a stream of a mixture of $N_3P_3F_6$, $N_3P_3F_5Cl$, $N_3P_3F_4Cl_2$, and $N_3P_3F_3Cl_3$ was discharged. The fire was immediately extinguished.

The present invention has been described and illustrated with reference to certain preferred embodiments. Nevertheless, it will be understood that various modifications, alterations and substitutions may be apparent to one of ordinary skill in the art, and that such modifications, alterations and substitutions may be made without departing from the essential invention. Accordingly, the present invention is defined by the following claims.

Claims:

1. The method of extinguishing or suppressing a fire in a total-flood application, characterized by the steps of

a) providing an agent containing at least one phosphorus nitride compound,

b) disposing said agent in a pressurized discharge system, and

c) discharging said agent into an area to provide an average resulting concentration in said area of between 0.1 and 12 percent by gas volume to extinguish or suppress fires in that area.

2. The method of claim 1 characterized in that said agent comprises at least one phosphorus nitride compound with one or more substituents selected from the group consisting of fluorine (F), chlorine (Cl), bromine (Br), iodine (I), imino (=NH), alkyls, substituted alkyls, aryls, substituted aryls, alkoxides, and substituted alkoxides.

3. The method of claim 2 characterized in that said substituted alkyls and substituted aryls are CH_2F, CHF_2, CF_3, CH_2CF_3, CF_2CF_3, and C_6F_5.

4. The method of claim 1 characterized in that said agent comprises one or more compounds selected from the group consisting of the cyclic compounds $P_3N_3Cl_6$, $P_3N_3ClF_5$, $P_3N_3Cl_2F_4$, $P_3N_3Cl_3F_3$, $P_3N_3Cl_4F_2$, $P_3N_3Cl_5F$, $P_3N_3F_6$, $P_4N_4Cl_8$, $P_4N_4Cl_7F$, $P_4N_4Cl_6F_2$, $P_4N_4Cl_5F_3$, $P_4N_4Cl_4F_4$, $P_4N_4Cl_3F_5$, $P_4N_4Cl_2F_6$, $P_4N_4ClF_7$, and $P_4N_4F_8$.

5. The method of claim 1 characterized by the step of adding to said agent a carrier comprised of one or more halocarbons.

6. The method of claim 5 characterized in that said at least one halocarbon is selected from the group consisting of hydrochlorofluorocarbons, hydrofluorocarbons, and perfluorocarbons.

7. The method of claim 6 characterized in that said hydrochlorofluorocarbons, hydrofluorocarbons, and perfluorocarbons contain 1 through 10 carbon atoms.

8. The method of claim 5 characterized in that said at least one halocarbon is selected from the group consisting of 2,2-dichloro-1,1,1-

trifluoroethane ($CHCl_2CF_3$), chlorodifluoromethane ($CHClF_2$), 2-chloro-1,1,1,2-tetrafluoroethane ($CHClFCF_3$), 1-chloro-1,1-difluoroethane (CH_3CClF_2), trifluoromethane (CHF_3), difluoromethane (CH_2F_2), 1,1-difluoroethane (CH_3CHF_2), pentafluoroethane (CHF_2CF_3), 1,1,1,2-tetrafluoroethane (CH_2FCF_3), 1,1,1,2,2-pentafluoropropane ($CF_3CF_2CH_3$), 1,1,1,2,3,3-hexafluoropropane ($CF_3CHFCHF_2$), 1,1,1,3,3,3-hexafluoropropane ($CF_3CH_2CF_3$), 1,1,1,2,2,3,3-heptafluoropropane ($CF_3CF_2CF_2H$), 1,1,1,2,3,3,3-heptafluoropropane (CF_3CHFCF_3), 1,1,1,4,4,4-hexafluorobutane ($CF_3CH_2CH_2CF_3$), tetrafluoromethane (CF_4), hexafluoroethane (CF_3CF_3), octafluoropropane ($CF_3CF_2CF_3$), decafluorobutane ($CF_3CF_2CF_2CF_3$), dodecafluoropentane ($CF_3CF_2CF_2CF_2CF_3$), tetradecafluorohexane ($CF_3CF_2CF_2CF_2CF_2CF_3$), perfluoromethylcyclohexane ($C_6F_{11}CF_3$), perfluorodimethylcyclohexane ($C_6F_{10}(CF_3)_2$), and perfluoromethyldecalin ($C_{10}F_{17}CF_3$).

9. The method of extinguishing or suppressing a fire in a streaming application, characterized by the steps of

a) providing an agent containing at least one phosphorus nitride compound,

b) disposing said agent in a pressurized discharge system, and

c) discharging said agent from said system toward an existing fire to suppress or extinguish said fire.

10. The method of claim 9 characterized in that said agent comprises at least one phosphorus nitride compound with one or more substituents selected from the group consisting of fluorine (F), chlorine (Cl), bromine (Br), iodine (I), imino (=NH), alkyls, substituted alkyls, aryls, substituted aryls, alkoxides, and substituted alkoxides.

11. The method of claim 10 characterized in that said substituted alkyls and substituted aryls are CH_2F, CHF_2, CF_3, CH_2CF_3, CF_2CF_3, and C_6F_5.

12. The method of claim 9 characterized in that said agent comprises one or more compounds selected from the group consisting of the cyclic compounds $P_3N_3Cl_6$, $P_3N_3ClF_5$, $P_3N_3Cl_2F_4$, $P_3N_3Cl_3F_3$, $P_3N_3Cl_4F_2$, $P_3N_3Cl_5F$,

$P_3N_3F_6$, $P_4N_4Cl_8$, $P_4N_4Cl_7F$, $P_4N_4Cl_6F_2$, $P_4N_4Cl_5F_3$, $P_4N_4Cl_4F_4$, $P_4N_4Cl_3F_5$, $P_4N_4Cl_2F_6$, $P_4N_4ClF_7$, and $P_4N_4F_8$.

13. The method of claim 9 characterized by the step of adding to said agent a carrier comprised of one or more halocarbons.

14. The method of claim 13 characterized in that said at least one halocarbon is selected from the group consisting of hydrochlorofluorocarbons, hydrofluorocarbons, and perfluorocarbons.

15. The method of claim 14 characterized in that said hydrochlorofluorocarbons, hydrofluorocarbons, and perfluorocarbons contain 1 through 10 carbon atoms.

16. The method of claim 13 characterized in that said at least one halocarbon is selected from the group consisting of 2,2-dichloro-1,1,1-trifluoroethane ($CHCl_2CF_3$), chlorodifluoromethane ($CHClF_2$), 2-chloro-1,1,1,2-tetrafluoroethane ($CHClFCF_3$), 1-chloro-1,1-difluoroethane (CH_3CClF_2), trifluoromethane (CHF_3), difluoromethane (CH_2F_2), 1,1-difluoroethane (CH_3CHF_2), pentafluoroethane (CHF_2CF_3), 1,1,1,2-tetrafluoroethane (CH_2FCF_3), 1,1,1,2,2-pentafluoropropane ($CF_3CF_2CH_3$), 1,1,1,2,3,3-hexafluoropropane ($CF_3CHFCHF_2$), 1,1,1,3,3,3-hexafluoropropane ($CF_3CH_2CF_3$), 1,1,1,2,2,3,3-heptafluoropropane ($CF_3CF_2CF_2H$), 1,1,1,2,3,3,3-heptafluoropropane (CF_3CHFCF_3), 1,1,1,4,4,4-hexafluorobutane ($CF_3CH_2CH_2CF_3$), tetrafluoromethane (CF_4), hexafluoroethane (CF_3CF_3), octafluoropropane ($CF_3CF_2CF_3$), decafluorobutane ($CF_3CF_2CF_2CF_3$), dodecafluoropentane ($CF_3CF_2CF_2CF_2CF_3$), tetradecafluorohexane ($CF_3CF_2CF_2CF_2CF_2CF_3$), perfluoromethylcyclohexane ($C_6F_{11}CF_3$), perfluorodimethylcyclohexane ($C_6F_{10}(CF_3)_2$), and perfluoromethyldecalin ($C_{10}F_{17}CF_3$).

17. The method of suppressing an explosion with an agent, characterized by the steps of

a) providing an agent containing at least one phosphorus nitride compound,

b) disposing said agent in a pressurized discharge system, and

c) detecting an explosion and discharging said agent into the area of the explosion to provide an average resulting concentration between 0.3 and 50 percent by gas volume to suppress the explosion.

18. The method of claim 17 characterized in that said agent comprises at least one phosphorus nitride compound with one or more substituents selected from the group consisting of fluorine (F), chlorine (Cl), bromine (Br), iodine (I), imino (=NH), alkyls, substituted alkyls, aryls, substituted aryls, alkoxides, and substituted alkoxides.

19. The method of claim 18 characterized in that said substituted alkyls and substituted aryls are CH_2F, CHF_2, CF_3, CH_2CF_3, CF_2CF_3, and C_6F_5.

20. The method of claim 17 characterized in that said agent comprises one or more compounds selected from the group consisting of the cyclic compounds $P_3N_3Cl_6$, $P_3N_3ClF_5$, $P_3N_3Cl_2F_4$, $P_3N_3Cl_3F_3$, $P_3N_3Cl_4F_2$, $P_3N_3Cl_5F$, $P_3N_3F_6$, $P_4N_4Cl_8$, $P_4N_4Cl_7F$, $P_4N_4Cl_6F_2$, $P_4N_4Cl_5F_3$, $P_4N_4Cl_4F_4$, $P_4N_4Cl_3F_5$, $P_4N_4Cl_2F_6$, $P_4N_4ClF_7$, and $P_4N_4F_8$.

21. The method of claim 17 characterized by the step of adding to said agent a carrier comprised of one or more halocarbons.

22. The method of claim 21 characterized in that said at least one halocarbon is selected from the group consisting of hydrochlorofluorocarbons, hydrofluorocarbons, and perfluorocarbons.

23. The method of claim 22 characterized in that said hydrochlorofluorocarbons, hydrofluorocarbons, and perfluorocarbons contain 1 through 10 carbon atoms.

24. The method of claim 21 characterized in that said at least one halocarbon is selected from the group consisting of 2,2-dichloro-1,1,1-trifluoroethane ($CHCl_2CF_3$), chlorodifluoromethane ($CHClF_2$), 2-chloro-1,1,1,2-tetrafluoroethane ($CHClFCF_3$), 1-chloro-1,1-difluoroethane (CH_3CClF_2), trifluoromethane (CHF_3), difluoromethane (CH_2F_2), 1,1-difluoroethane (CH_3CHF_2), pentafluoroethane (CHF_2CF_3), 1,1,1,2-tetrafluoroethane (CH_2FCF_3), 1,1,1,2,2-pentafluoropropane ($CF_3CF_2CH_3$), 1,1,1,2,3,3-hexafluoropropane ($CF_3CHFCHF_2$), 1,1,1,3,3,3-hexafluoropropane ($CF_3CH_2CF_3$), 1,1,1,2,2,3,3-heptafluoropropane ($CF_3CF_2CF_2H$), 1,1,1,2,3,3,3-

heptafluoropropane (CF_3CHFCF_3), 1,1,1,4,4,4-hexafluorobutane ($CF_3CH_2CH_2CF_3$), tetrafluoromethane (CF_4), hexafluoroethane (CF_3CF_3), octafluoropropane ($CF_3CF_2CF_3$), decafluorobutane ($CF_3CF_2CF_2CF_3$), dodecafluoropentane ($CF_3CF_2CF_2CF_2CF_3$), tetradecafluorohexane ($CF_3CF_2CF_2CF_2CF_2CF_3$), perfluoromethylcyclohexane ($C_6F_{11}CF_3$), perfluorodimethylcyclohexane ($C_6F_{10}(CF_3)_2$), and perfluoromethyldecalin ($C_{10}F_{17}CF_3$).

25. The method of inerting an area to prevent a fire or explosion, characterized by the steps of

a) providing an agent containing at least one phosphorus nitride compound,

b) disposing said agent in a pressurized discharge system, and

c) discharging said agent into said area to provide an average resulting concentration between 1 and 13 percent by gas volume to prevent a fire or an explosion from occurring.

26. The method of claim 25 characterized in that said agent comprises at least one phosphorus nitride compound with one or more substituents selected from the group consisting of fluorine (F), chlorine (Cl), bromine (Br), iodine (I), imino (=NH), alkyls, substituted alkyls, aryls, substituted aryls, alkoxides, and substituted alkoxides.

27. The method of claim 26 characterized in that said substituted alkyls and substituted aryls are CH_2F, CHF_2, CF_3, CH_2CF_3, CF_2CF_3, and C_6F_5.

28. The method of claim 25 characterized in that said agent comprises one or more compounds selected from the group consisting of the cyclic compounds $P_3N_3Cl_6$, $P_3N_3ClF_5$, $P_3N_3Cl_2F_4$, $P_3N_3Cl_3F_3$, $P_3N_3Cl_4F_2$, $P_3N_3Cl_5F$, $P_3N_3F_6$, $P_4N_4Cl_8$, $P_4N_4Cl_7F$, $P_4N_4Cl_6F_2$, $P_4N_4Cl_5F_3$, $P_4N_4Cl_4F_4$, $P_4N_4Cl_3F_5$, $P_4N_4Cl_2F_6$, $P_4N_4ClF_7$, and $P_4N_4F_8$.

29. The method of claim 25 characterized by the step of adding to said agent a carrier comprised of one or more halocarbons.

30. The method of claim 29 characterized in that said at least one halocarbon is selected from the group consisting of hydrochlorofluorocarbons, hydrofluorocarbons, and perfluorocarbons.

31. The method of claim 30 characterized in that said hydrochlorofluorocarbons, hydrofluorocarbons, and perfluorocarbons contain 1 through 10 carbon atoms.

32. The method of claim 29 characterized in that said at least one halocarbon is selected from the group consisting of 2,2-dichloro-1,1,1-trifluoroethane ($CHCl_2CF_3$), chlorodifluoromethane ($CHClF_2$), 2-chloro-1,1,1,2-tetrafluoroethane ($CHClFCF_3$), 1-chloro-1,1-difluoroethane (CH_3CClF_2), trifluoromethane (CHF_3), difluoromethane (CH_2F_2), 1,1-difluoroethane (CH_3CHF_2), pentafluoroethane (CHF_2CF_3), 1,1,1,2-tetrafluoroethane (CH_2FCF_3), 1,1,1,2,2-pentafluoropropane ($CF_3CF_2CH_3$), 1,1,1,2,3,3-hexafluoropropane ($CF_3CHFCHF_2$), 1,1,1,3,3,3-hexafluoropropane ($CF_3CH_2CF_3$), 1,1,1,2,2,3,3-heptafluoropropane ($CF_3CF_2CF_2H$), 1,1,1,2,3,3,3-heptafluoropropane (CF_3CHFCF_3), 1,1,1,4,4,4-hexafluorobutane ($CF_3CH_2CH_2CF_3$), tetrafluoromethane (CF_4), hexafluoroethane (CF_3CF_3), octafluoropropane ($CF_3CF_2CF_3$), decafluorobutane ($CF_3CF_2CF_2CF_3$), dodecafluoropentane ($CF_3CF_2CF_2CF_2CF_3$), tetradecafluorohexane ($CF_3CF_2CF_2CF_2CF_2CF_3$), perfluoromethylcyclohexane ($C_6F_{11}CF_3$), perfluorodimethylcyclohexane ($C_6F_{10}(CF_3)_2$), and perfluoromethyldecalin ($C_{10}F_{17}CF_3$).

INTERNATIONAL SEARCH REPORT	International application No. PCT/US95/12602

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :A62C 2/00, 3/00; A62D 1/00, 1/02, 1/06, 1/08
US CL : 169/45, 46, 47; 252/2, 3, 4, 8
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 169/45, 46, 47; 252/2, 3, 4, 8

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS TEXT SEARCH, STN/CAS ONLINE

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 4,053,560 (GARNER) 11 October 1977, see abstract, and column 1, line 50 to column 2, line 59.	1-31
Y	US, A, 3,867,344 (FRANK ET AL.) 18 February 1975, see abstract, and column 1, line 65 to column 2, line 66.	1-31
Y	US, A, 3,974,251 (CREMER ET AL.) 10 August 1976, see abstract and column 2, lines 18-42.	1-31
Y	US, A, 4,063,883 (HUPFL ET AL.) 20 December 1977, see abstract.	1-31
Y	US, A, 5,135,054 (NIMITZ ET AL.) 04 August 1992, see abstract, and claims 1-2.	1-16

[X] Further documents are listed in the continuation of Box C. [ ] See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E"	earlier document published on or after the international filing date		
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed	"&"	document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
02 JANUARY 1996	22 JAN 1996
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230	Authorized officer JOSEPH D. ANTHONY Telephone No. (703) 308-1235

Form PCT/ISA/210 (second sheet)(July 1992)*

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US95/12602

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 5,102,557 (NIMITZ ET AL.) 07 April 1992, see abstract, and claims 1-4.	1-16
Y	US, A, 4,903,573 (BROWNE ET AL.) 27 February 1990, see abstract, examples 1-2 and claims 1-7.	17-31
Y	US, A, 4,722,766 (SPRING) 02 February 1988, see abstract, column 1, line 50 to column 2, line 60, and claims 1-12.	17-31